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Debabrata Mukherjee

Iowa State University, debu@iastate.edu

Arkady Ellern

Iowa State University, ellern@iastate.edu

Aaron D. Sadow

Iowa State University, sadow@iastate.edu

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Abstract

An unusual β -elimination reaction involving zinc(II) and LiCl is reported. LiCl and a coordinatively saturated disilazido zinc compound form an adduct that contains activated SiH moieties. In THF/toluene mixtures, this adduct is transformed into a zinc hydride and 0.5 equiv. cyclodisilazane. The Li⁺ and Cl⁻ ions apparently affect the reaction pathway of the disilazido zinc in a synergistic fashion. Thus, the zinc hydride and cyclodisilazane products of formal β -elimination are not observed upon treatment of the zinc disilazide with Cl⁻ or Li⁺ separately.

Keywords

Elimination reaction, Reaction pathways, zinc compounds, disilazane, lithium chloride, silane derivative, silicon, tetrahydrofuran, toluene, biotransformation, crystal structure, cycloaddition, ion transport

Disciplines

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Conversion of a Zinc Disilazide to a Zinc Hydride Mediated by LiCl

Debabrata Mukherjee, Arkady Ellern, and Aaron D. Sadow*

Department of Chemistry and U.S. Department of Energy Ames Laboratory, Iowa State University, Ames, Iowa 50011

Received March 19, 2010; E-mail: sadow@iastate.edu

Organozinc compounds are valuable in synthetic chemistry as alkyl, aryl, and hydride transfer agents that complement organolithium and organomagnesium reagents.¹ Importantly, alkali metal and alkaline earth metal salt adducts of zinc reagents give selective group transfer chemistry that is distinct from monometallic main group reagents, and related adducts facilitate selective arene, hydrocarbon, and alkylether metalations.² Zn(II) centers also mediate physiological processes involving group transfer as in liver alcohol dehydrogenase (LADH), where hydride transfer from a zinc alkoxide to NAD⁺ is proposed.³ A connection between synthetic and physiological zinc chemistry is provided by molecular coordination complexes such as tris(pyrazolyl)borato zinc alkoxides and hydroxide that model LADH,⁴ carbonic anhydrase,⁵ and phosphatase.⁶ Likewise, hydrolase-like transesterifications are catalyzed by tris-1,1,1-(oxazolonyl)ethane zinc dicarboxylate and ditriflate compounds for kinetic resolution of chiral esters.⁷

Given the importance of zinc-mediated group transfer chemistry, it is interesting that β -hydrogen elimination is not a common pathway for organozinc compounds. For example, ZnEt₂ undergoes β -elimination only upon IR laser pyrolysis at 600–650 °C, whereas thermal treatment results in Zn–C bond homolysis.⁸ Few solution phase β -eliminations have been suggested, most notably in the thermolysis of [NaZnEt₃] under reducing conditions.⁹ A three-coordinate diketiminato zinc hydride is prepared from the corresponding zinc chloride and KNH*i*-PrBH₃ via an unobserved amido-BH₃ intermediate.¹⁰ β -Elimination was also proposed as an initiation step in a zinc-catalyzed ketone hydrosilylation.¹¹ Identification of conditions that favor or disfavor β -H elimination in zinc(II) compounds may have important implications in group transfer reactions in synthetic and enzymatic chemistry. Here, we report a coordinatively saturated oxazolonylborato disilazidozinc(II) compound that undergoes a formal β -H elimination at room temperature facilitated by LiCl.

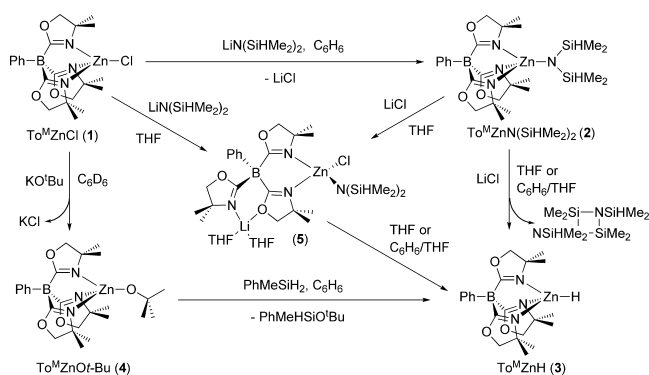
Treatment of To^MZnCl (**1**) (To^M = tris(4,4-dimethyl-2-oxazolonyl)phenylborate) with LiN(SiHMe₂)₂ in benzene readily provides To^MZnN(SiHMe₂)₂ (**2**), and no other products are detected by ¹H NMR spectroscopy before or after workup. The spectroscopic features of the SiH, including its downfield chemical shift (5.26 ppm), high ¹J_{SiH} (185 Hz), and ν_{SiH} (2110 cm⁻¹), are consistent with a normal disilazido ligand. An X-ray crystal structure (see Supporting Information) contains Zn···H and Zn···Si distances (2.98 Å and 3.06 Å) that are longer than the sums of van der Waals radii.

Although **2** is formed quantitatively in benzene, in a benzene (10 mL) and THF (2 mL) mixture, the compounds **2**, **1**, and To^MZnH (**3**) (identified later) are present in a ratio of 20:1:8 upon workup after 24 h. Additionally, 1,3-diaza-2,4-disilacyclobutane (Me₂HSiN–SiMe₂)₂,¹² is observed. This cyclodisilazane is the head-to-tail dimer of silaimine Me₂HSiN=SiMe₂; its formation and the presence of zinc hydride **3** suggest a β -elimination reaction. Reactions of lithium hydrosilazides and group 14 electrophiles (e.g.,

Me₃SiCl) in hexane give cyclodisilazanes, and silaimines are suggested as intermediates in one of the two proposed mechanisms.¹² These literature transformations require nonpolar media, and THF solvent gives substitution rather than elimination. Our zinc system contrasts with that of Me₃SiCl, with nonpolar solvents giving substitution and THF favoring elimination. Neither HN(SiHMe₂)₂ and LiCl nor mixtures of **1**, HN(SiHMe₂)₂, and LiCl afford the cyclodisilazane.

The identity of zinc hydride **3** is provided by its independent preparation in a two-step sequence. Reaction of **1** and KO*t*-Bu provides To^MZnO*t*-Bu (**4**). As shown in Scheme 1, PhMeSiH₂

Scheme 1. LiCl Adduct Formation, β -Elimination and Independent Synthesis of To^MZnH



and **4** react to give **3**. Notably, **2** and PhMeSiH₂ do not readily provide **3**, presumably due to the hindered, non-nucleophilic nature of the zinc disilazide. The IR spectrum of **3** contains a ν_{ZnH} (1745 cm⁻¹, KBr), and the ZnH resonance appears at 4.29 ppm in the ¹H NMR spectrum (cf. HB(3-*i*Bupz)₃ZnH, δ_{ZnH} 5.36; ν_{ZnH} 1770 cm⁻¹).¹³ A single crystal X-ray diffraction study reveals that **3** is monomeric and contains a terminal zinc hydride, of which there are relatively few crystallographically studied examples including the four-coordinate Tp^{*t*Bu}ZnH and Tp^{*Ph*,*Me*}ZnH (for which the ZnH are not located)¹³ and a three-coordinate diketiminate ZnH (Zn–H 1.46(2) Å).¹⁰ The four-coordinate ZnH in **3** (1.52(2) Å) is longer by 0.06 Å.

LiN(SiHMe₂)₂ and **1** react in THF-*d*₈ to provide possible intermediates in the apparent β -elimination process. Two C_s-symmetric compounds are detected after 10 min, rather than C_{3v}-symmetric **1**, **2**, and **3**. After 12 h at room temperature, the minor species is partly converted into **3** and (Me₂HSiN–SiMe₂)₂. Attempts to isolate these intermediates from toluene/THF solvent mixtures (crystallization conditions) afford crystals of **3**.

We suspected that the intermediates formed from **1** and LiN(SiHMe₂)₂ in THF were LiCl adducts. Therefore, LiCl and zinc disilazide **2** were allowed to interact. A crystallized sample of the 1:1 LiCl/**2** adduct (**5**) has the same ¹H NMR spectrum as 1:1

$\text{LiN}(\text{SiHMe}_2)_2/\mathbf{1}$ (major isomer). The ν_{SiH} of this material is lower (2061 cm^{-1}) than in the case of **2**, and the $^1J_{\text{SiH}}$ (102 Hz) is significantly lower. Compound **5** is fluxional, as it crystallizes at $-80\text{ }^\circ\text{C}$ from THF with a C_1 -symmetric structure (Figure 1). Although spectroscopic features suggest $[\text{M}]-\text{SiH}$ interactions, there are no close contacts between the SiH moieties and the Zn or Li centers in **5**. Additionally, this interesting structure contains an unusual $O\text{-Li}\cdots\text{N}\cdots\text{Zn}$ -coordinated bridging oxazoline group. The phenyl group on boron and the chloride on zinc are disposed *syn*, as are the N -lithiated oxazoline and $\text{N}(\text{SiHMe}_2)_2$ groups. Because Li^+ and Cl^- are separate in **5**, we investigated these ions independently to determine their role in the formal β -elimination.

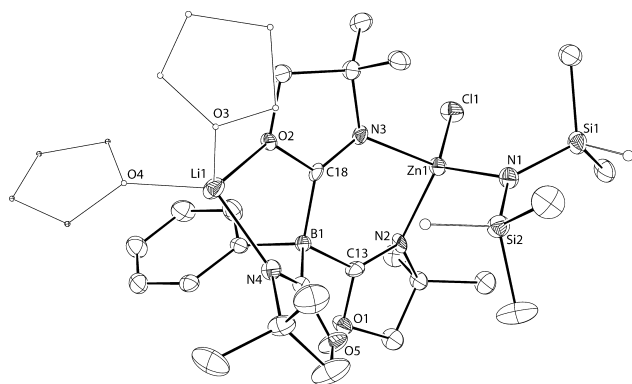
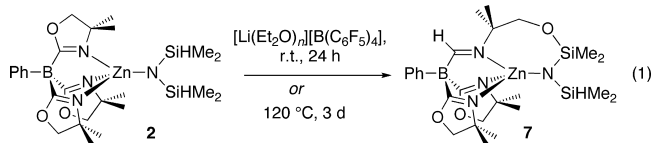


Figure 1. ORTEP diagram of **5** drawn at 35% probability.

Treatment of **2** with $[\text{n-Bu}_4\text{N}]\text{Cl}$ in a mixture of benzene- d_6 and THF- d_8 also gives two C_s -symmetric species. One of the isomers crystallizes and was structurally characterized as $[\text{n-Bu}_4\text{N}][(\kappa^2\text{-To}^{\text{M}})\text{-ZnClN}(\text{SiHMe}_2)_2]$ (**6**). The IR spectrum (KBr) of **6** shows a broad, intense ν_{SiH} at 2036 cm^{-1} which is notably lower energy than in the case of **2** (2110 cm^{-1}) and **5** (2061 cm^{-1}). The $^1J_{\text{SiH}}$ values in **6** (178 Hz) are slightly lower than in the case of **2** (185 Hz). After 1 week, neither **3** nor $(\text{Me}_2\text{HSiN-SiMe}_2)_2$ is observed, and no change is detected in the ^1H NMR spectrum. Thus, although addition of Cl^- affects the ν_{SiH} of the disilazide, it does not promote β -elimination from the Zn(II) amide.

Addition of $[\text{Li}(\text{Et}_2\text{O})_n][\text{B}(\text{C}_6\text{F}_5)_4]$ to **2** in benzene- d_6 /THF- d_8 mixtures results in oxazoline ring-opening giving O-Si bond formation and formal transfer of hydrogen from silicon to the (former) imidine carbon (eq 1).



A bimolecular transformation, in which a Zn-N bond of **5** reacts with a Si-H bond of a second molecule, might also explain the $\beta\text{-H}$ elimination chemistry. However, THF- d_8 solutions of **5** and Et_3SiH (as a competitive tertiary SiH group) give $\text{To}^{\text{M}}\text{ZnH}$ and cyclodisilazane, while the Et_3SiH is unreacted. Also, only starting materials are observed upon treatment of **2** with Et_3SiH , ruling out an intermolecular dehydrocoupling-type mechanism.

Clearly, Li^+ and Cl^- have a synergistic effect in this β -elimination reaction through the formation of the adduct **5**, and this requirement is surprising given the coordinative and electronic

saturation in both **2** and **5**. It is tempting to suggest that Cl^- dissociation from **5** gives a three-coordinate zinc center that undergoes β -elimination. However, such a mechanism requires an unlikely $2\times$ repetition of a Cl^- coordination and dissociation sequence since the final product, $\text{To}^{\text{M}}\text{ZnH}$, does not form a detectable adduct with LiCl , and Cl^- appears to be necessary to inhibit oxazoline ring-opening. Cl^- also does not appear to bind to silicon, as H-transfer is not observed in the absence of Li^+ . Furthermore, addition of the Lewis acids BPh_3 or $\text{B}(\text{C}_6\text{F}_5)_3$ to **6** does not provide cyclodisilazane, suggesting that Li^+ is not acting as a Lewis acid in **5** to mediate hydride transfer.

Lithium chloride also affects the electronic properties of the disilazide ligand, as shown by the spectroscopy of the $\beta\text{-SiH}$ moiety. This electronic effect may be more significant than a low coordination number for zinc because the dicoordinate $\text{ZnN}(\text{SiHMe}_2)_2$ is not reported to undergo β -elimination.¹⁴ Therefore, we favor a mechanism in which the zinc hydride is formed from the four-coordinate $[(\kappa^2\text{-To}^{\text{M}})\text{ZnClN}(\text{SiHMe}_2)_2]^-$. Given the importance of Zn-mediated reactions in synthetic, catalytic, and enzymatic chemistry, we are currently investigating related zinc amido, alkyl, and alkoxide compounds in $\beta\text{-H}$ and group transfer reactions.

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Supporting Information Available: Experimental procedures and crystallographic data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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